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OPTIMIZATION OF SYNTHESIS OF ALUMINUM HYDROXIDES AND HIGHLY-DISPERSE ALUMINUM OXIDE

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The results of producing highly-disperse cubic aluminum oxide by the chemical precipitation method from aluminum hydroxide solutions with subsequent dehydration are described.

Among the most promising 21st century materials are ceramics, in particular, aluminum oxide and corundum ceramics based on aluminum oxide. The cubic forms of aluminum oxide, which are the basis of active aluminum oxide, are of special interest. This material is used as absorbent, catalyst carrier, or catalyst of chemical processes. New technologies are currently being developed that use highly disperse and highly pure initial materials. The development of new synthesis methods will make it possible to significantly increase the adsorption capacity and improve other properties of active aluminum oxide.

The purpose of the present study was to obtain highly disperse cubic aluminum oxide by chemical precipitation from aluminum hydroxide solutions with subsequent dehydration and to identify the effect of the process parameters on the dispersion and phase transformation of aluminum hydroxides and oxide.

The scheme of aluminum hydroxide production included the preparation of an initial solution of aluminum-containing salts and precipitators of a preset concentration, mixing of solutions and intense stirring of the reaction mixture with an magnetic agitator for 10 min, separation of the matrix solution from the precipitate, triple washing of the precipitate with water, vacuum or centrifuge filtration, and drying of the precipitate. High-dispersion cubic aluminum oxide was obtained by dehydration of the synthesized aluminum hydroxides in an electric furnace. The temperature conditions of firing were selected based on the DTA data. The specific surface area of the powders was determined by the BET method, and their phase composition was identified by x-ray phase analysis.

The study included the following aspects:

– optimization of the conditions of precipitating aluminum hydroxide (pH in precipitation, type of aluminum-bearing precursor and precipitator, concentration of initial solutions);

– study of the phase composition and dispersion of aluminum hydroxide and oxide;

– study of the effect of additives (mostly metal chlorides) on precipitation of hydroxides.

To select the pH of the medium, synthesis was first carried out in microvolumes and calibration curves were constructed, based on which it was decided to conduct experiments in three ranges: alkaline, neutral, and acid.

The precipitates obtained in a neutral medium at pH = 7 – 8 are a mixture of two aluminum hydroxides: bayerite and boehmite. In some cases, only boehmite or an x-ray-amorphous precipitate was registered. The thermograms of these precipitates do not exhibit clearly expressed endothermic effects correlating with dehydration of aluminum hydroxide. Some thermograms exhibit endothermic effects of weak intensity.

Introduction of stabilizing additives into the reaction mixture in some cases modifies the phase composition of the precipitates and changes the shape of their thermograms.

Analysis of obtained results makes it possible to split the additives investigated into three groups:

– $BaCl_2$ and $NiCl_2$ stabilize the formation of well-crystallized bayerite in an alkaline medium regardless of the type of the aluminum-containing precursor ($AlCl_3$, $Al(NO_3)_3$);

– LiOH facilitates the formation of partly amorphous (poorly crystallized) bayerite under any precipitation conditions;

– $FeCl_3$, $MgCl_2$, and $LaBr_2$ manifest different effects under different precipitation conditions.

It is noted that the magnesium chloride additive facilitates the formation of well-crystallized bayerite when NH_4OH is used as a precipitator, or the formation of poorly crystallized bayerite or the amorphous precipitate when KOH is used.

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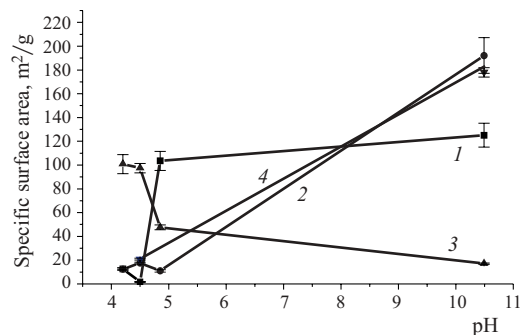
Fig. 1. Variation of the specific surface area of η-Al$_2$O$_3$ depending on the pH of the medium using AlCl$_3$: *1*) AlCl$_3$ + NaOH; *2*) AlCl$_3$ + KOH; *3*) AlCl$_3$ + LiOH; *4*) AlCl$_3$ + NH$_4$OH.
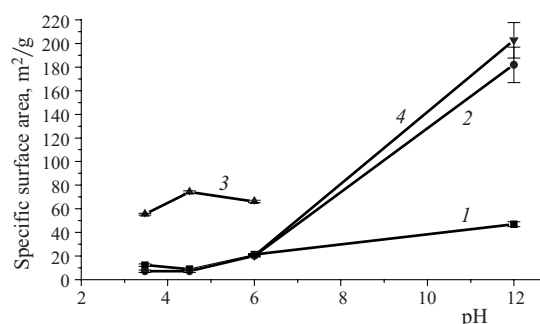

Fig. 2. Variation of the specific surface area of η-Al$_2$O$_3$ depending on the pH of the medium using Al(NO$_3$)$_3$: *1*) Al(NO$_3$)$_3$ + NaOH; *2*) Al(NO$_3$)$_3$ + KOH; *3*) Al(NO$_3$)$_3$ + LiOH; *4*) Al(NO$_3$)$_3$ + NH$_4$OH.

Thus, introduction of stabilizing additives to a certain extent makes it possible to control the phase composition of aluminum hydroxide precipitate. It is recommended to use barium and nickel chlorides as additives stabilizing the process of crystallization of bayerite. The stabilizing effect of these additives is presumably related to their participation in the construction of the crystalline lattice of aluminum hydroxide.

The variation curves of the specific surface area of η-Al$_2$O$_3$ depending on the pH in using various precipitators were constructed in the course of experiments (Fig. 1).

All curves can be split into there groups.

In the case of AlCl$_3$, the variation curves of specific surface area using NH$_4$OH and KOH as precipitators can be classified as the first group. The shape of these curves is identical: with increasing pH, the dispersion grows and reaches 160 – 180 m^2/g (pH = 10.5).

The second group includes the dependences of the specific surface area of η-Al$_2$O$_3$ using NaOH as a precipitator.

In this case a sharp increase in the specific surface area (100 m^2/g) is observed in the range of pH = 5, and with a further increase in pH, the dispersion grows insignificantly (to 120 m^2/g).

The dependence of the specific area of η-Al$_2$O$_3$ with LiOH as a precipitator can be regarded as the third group. In this case, the maximum value of the specific surface area is reached in an acid medium. Upon passing to an alkaline medium, the dispersion decreases.

The situation with aluminum nitrate (Fig. 2) is similar to that of aluminum chloride. The maximum dispersion using KOH and NH$_4$OH is reached in an alkaline medium, when NaOH is used, the specific surface area is somewhat smaller, and with LiOH, the maximum value is reached in an acid medium and decreases with an increasing pH.

In both cases (aluminum nitrate and chloride), one can trace the dependence of the specific surface area of η-Al$_2$O$_3$ on the radius of the cation of the alkaline precipitator metal. It can be assumed that as the cation radius in the series of Li$^+$ → Na$^+$ → K$^+$ → NH$_4^+$ grows, the interlayer between the Al(OH)$_3$ molecules in the solution increases. As a result, the coagulation of the molecules at the moment of their formation is impeded, since there is no direct contact between the particles. In the case of using cations with a small radius, coagulation of Al(OH)$_3$ takes place. With increasing cation radius, the specific surface area of the resulting η-Al$_2$O$_3$ attains higher values.

In using 5N solution, the dispersion significantly increases even in an acid medium compared with 1N solution. When aluminum chloride is used as the aluminum-bearing component, the dispersion reaches 250 m^2/g. In using 5N solution of aluminum nitrate, the specific surface area grows significantly faster within the interval of pH = 4 – 10 than in using 1N solution. However, the experiments with 5N solutions could not guarantee obtaining a preset value of pH, which is evidence of the greater sensitivity of the system.

Thus, highly dispersed aluminum hydroxides were obtained and crystalline aluminum oxide of the cubic modification was produced based on them.

The performed studies made it possible to optimize the technological parameters of the synthesis of high-disperse cubic aluminum oxide using the precipitation method:

– the aluminum-bearing component can be either aluminum chloride or aluminum nitrate;

– the precipitator can be a 5% solution of NH$_4$OH or 1N solution of KOH, and an alkaline medium with pH = 10 – 11;

– to stabilize the formation of aluminum hydroxide in the form of bayerite, it is recommended to used barium chloride or nickel chloride additives in the amount of 5%.